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Computer-Assisted Furnace Atomic Absorption Spectrometric Analysis

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16 ABSTRACT

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Computer-Assisted Furnace Atomic Absorption Spectrometric Analysis

by J.E. Feldsott

The use of furnace atomic absorption instrumentation with a two-key chromate/methyl ester system is described. A simple addition of relays to the furnace power supply allows for automatic start-up of A/D conversion and spectrophotometer zeroing at the proper time. Manipulations involving editing, zeroing and averaging of up to 250 absorption signals in an analysis run were accomplished by developing a procedure employing basic hardware programming techniques. The same dedicated data system was employed for all steps and post-run data processing, conveniently accomplished in 5-10 minutes, gave a tabulation of sample name, mean concentration, standard deviation, number of analyses, and percent recovery.

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The coprecipitation behavior of manganese and nickel is interesting. In the case of manganese, filtration of the insoluble hydrated oxides removes most manganese (sample 3), but the acidification treatment leaves over 90% of the manganese in solution (sample 3). We suspect that in the former case, insoluble manganese dioxide is formed via oxidation by dissolved oxygen and is filtered off. In the latter case, the reduction step keeps manganese in the +2 oxidation state, which apparently remains in solution as an hydroxo complex. The precipitation of Ni(II) in sample 2 probably results from coprecipitation with other metal ions.

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JOURNAL ARTICLE

Computer-Assisted Furnace Atomic Absorption Spectrometric Analysis

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The popularity of furnace atomic absorption spectrometry (FAAS) has resulted in the performance of an ever-increasing number of determinations by this method in environmental studies (1). In addition, this has precipitated studies of performance evaluations (2,3) for commercial instrumentation. Although high sensitivity is perhaps one of its most outstanding features, some well-known serious disadvantages are the lengthy times for analysis, including data analysis, and the presence of matrix interferences that necessitate the use of standard additions to samples.

Presently, there exists no readily available description of a data acquisition and handling method that is both flexible and designed to conveniently satisfy the specific needs of production analysis. The objective of this work is to report a method for using a turnkey data system with FAAS instrumentation. Use of the system's high-level language programming capabilities together with the peak integration software results in a combination providing both on-line and high-volume post-run calculation capabilities. As applied to natural water analysis, the following discussion will describe the performance of a particular instrumental configuration and a method for the acquisition and reduction of large numbers of atomization signals near instrumental detection limits.

EXPERIMENTAL

Apparatus. Atomic absorption instrumentation (Perkin-Elmer) consisted of a Model 305B atomic absorption spectrophotometer equipped with a deuterium arc background corrector, an HGA-2100 graphite furnace atomizer, and a Model 56 recorder. Hollow cathode lamps were employed for copper and lead analyses, and an electrodeless discharge lamp was used for cadmium. The argon gas was interrupted during atomization for lead, whereas the noninterrupted mode was used for cadmium and copper. Other operating conditions and trace analysis considerations are given elsewhere (4). In order to start the analog to digital (A/D) converter, an ultrasensitive SPDT relay (Hi-Mag Electrol was installed at pole 8 of the recorder switch on the HGA-2100 power supply (used in auto mode), as indicated in Figure 1. This allowed for A/D conversion to start automatically during the furnace program charring cycle by simply providing a contact closure about 15 s prior to the start of atomization. It was convenient that the charring time be set to any value greater than 15 s. An identical relay was installed in parallel with the aforementioned relay to provide contact closure for the terminals of the spectrophotometer auto zero control, except for during atomization and 15 s prior to it. This provided automatic instrument zeroing, and thus the 0 ± 10 mV baseline required for the computer was assured. Since it was advantageous to be able to manipulate the spectrophotometer baseline voltage from a value other than zero, a simple voltage offset (summing) circuit (5) was constructed from a low-cost operational amplifier (741HC, Fairchild) and was placed between the spectrophotometer output and the A/D input (Figure 9). As indicated, this circuit also provided for approximately 100-fold amplification to 5-fold deamplification of the signal from the spectrophotometer.

The computer hardware-software was a Model 5950B gas chromatography data system (Hewlett-Packard), which included 32K of core memory, a punch and reader-equipped HP 2752A teleprinter, a 9748B photo-tape reader, a 9866A line printer, an 1806 A remote A/D module, and the Lab BASIC language interpreter. A 1-V full-scale analog signal from the spectrophotometer was input to the A/D converter, which operated at a sampling rate of 32 Hz. This sampling rate was the highest available but it was sufficient to provide for accurate integration of relatively rapid atomization signals.

Programs and Procedure. All relevant analytical information is recorded on paper tape. If experiment identification information is desired, it is entered before all other data. The analysis sequence is begun by simply initiating a program cycle on the furnace. At the conclusion of each cycle, the system prints the current sample number, estimated concentration, and requests input for the sample code. The sample code indicates whether the injection is a standard, a sample, or a sample with a spike. A misentered sample number or code can be easily corrected.

The design of the post-run calculation requires that a set or any random number of sample or spiked sample injections be grouped during the analytical run since only consecutive signals for a sample are averaged. Each sample name is unique and possesses eight or less characters, either alpha or numeric, or both. The name BLK is reserved to indicate a general analysis blank that can be analyzed and subtracted from all samples in the analytical run. Corresponding spiked and unspiked samples require the same sample name and have to differ by the sample code which designates the concentration of the spike. The data manipulation scheme requires that any number of spiked samples immediately follow a particular sample in the analysis sequence to allow for calculation of the average recovery. Any

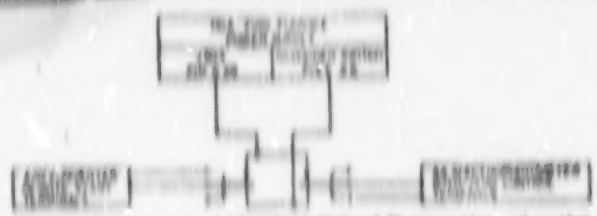

Figure 1. Arrangement of relays for initiating A/D conversion and sensing AA spectrophotometer prior to furnace atomization cycle

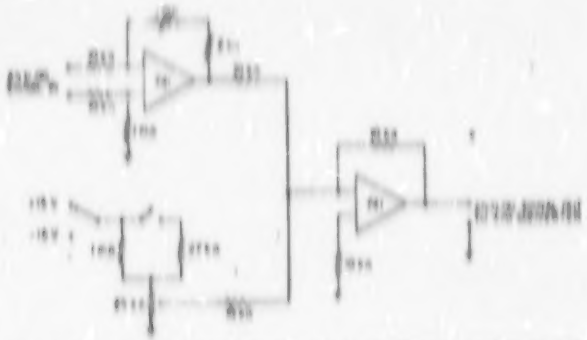

Figure 2. Circuit providing amplification and offset of analog voltage signal prior to input to A/D converter

sample name can be used for a standard, since only the sample code is employed for identifying and determining the nominal value of the standard. Standards can be injected at any time or in any order, including during the middle of a series of sample injections, without interrupting the averaging of values for samples. The last data-entry sequence on the paper tape is an end flag (sample code = −99). The maximum number of atomizations allowed is 200 because of storage limitations for this data system.

RESULTS AND DISCUSSION

Data Acquisition. Hewlett-Packard's method for obtaining the area under a single peak requires that the user supply values for certain parameters. With input of a calibration factor, the net result is the on-line calculation of sample concentration for each atomization peak. This explanation is well documented in the HP 9862 operation manual and any values specifically applicable to this experiment are available from the author. This method was used in conjunction with an auto-call BASIC program written to extract only the relevent information in proper format for punching on paper tape. The flow chart in Figure 3 explains duties of the BASIC program for both on-line and post-run operations. For each analysis sequence four items were recorded on paper tape: (1) sample name, (2) sample code, (3) peak area, and (4) calculated on-line concentration.

Post-Run Data Analysis. Data processing for FAAS production analyses is best accomplished in a post-run fashion, since contamination problems and other factors inherent in this type of analysis sometimes require an unpredictable number of sample injections, deletions of invalid data, standard additions to some samples for calibration, and blank corrections. The data processing scheme must therefore be as general and flexible as possible. However, designing a completely general scheme would require the use of several large data storage matrices for over 200 analysis sequences. On our dedicated computer system, capacity beyond the present available memory size for BASIC programs (~7K) was not available. The post-run calculation program required 6.5K of memory. Thus, the program was designed for relatively small data storage while still remaining flexible.

Initially, the program steps through the set of data points for each peak and selects only those points that are labeled as standards (Figure 1). The user may elect to automatically

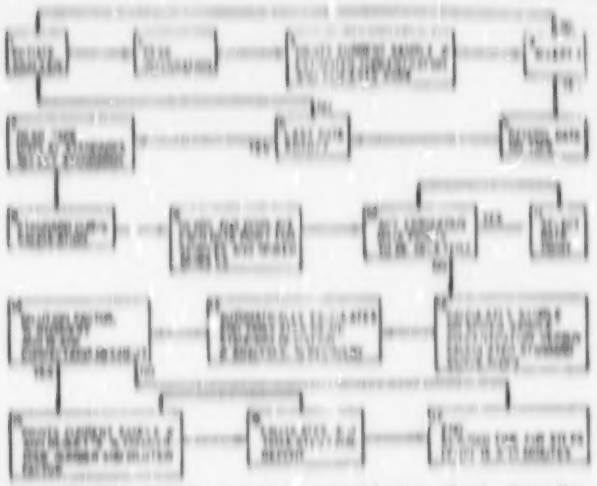

Figure 3. Flow chart for microcomputer-assisted furnace atomic absorption analysis

use all standards or he may step through each standard individually. If the latter is done, the data point is employed by typing the number 1 or deleted by typing 999. For all selected standards, a curve fit is performed using a 3-variable multiple linear regression analysis (6, 7) on the following second-order polynomial,

$$Y = a + bX + cX^2 \qquad (1)$$

where Y equals the nominal standard concentration and X equals the observed peak area. The zero-order, first-order, and second-order coefficients in addition to the multiple correlation coefficient are then calculated and displayed. Initial sample concentrations are first calculated on the basis of the slope. The second part consists of displaying all data generated for each sample, which the user then examines from which he selectively deletes any peaks that may be erroneous. Thirdly, automatic calculation and tabulation of the mean concentration, the standard deviation, the number of analyses, and the mean percent recovery can be later applied on selected samples are performed. The mean percent recovery is defined as

$$\sum_{i=1}^{n} \frac{100\,(SS_i - S)}{NS_i} \Big/ n \qquad (2)$$

where SS_i is the measured mean concentration of the ith spiked sample and S is the measured mean concentration of the unspiked sample, all relative to the constructed standard curve. The term NS_i is the nominal value of the ith spike for a sample, and n is the total number of spikes applied to a particular sample. Working within a linear range is especially desirable for FAAS; however, calculations do allow for the possibility of curvature. The fourth and final sequence is final report generation in which an analysis blank (BL1K), a user-specified recovery, and a dilution factor are used to calculate each final corrected sample concentration. The processing of one day's analytical run and report generation requires about 5–15 min, and the data tape may obviously be saved for any future reference or recalculation.

Application to Natural Water Analysis. In the analysis of natural waters, detection limits are frequently approached. This condition applies particularly to analyses of copper, cadmium, and lead in which the lower range of natural concentrations for unpolluted waters can be typically 1, 0.01, and 0.2 $\mu g/L$, respectively (4). This type of analysis therefore provided a useful and stringent test of the system.

The reliability of integration at relatively low but realistic concentrations with the maximum possible A/D sampling rate

Table I. Reproducibility and Correlation of Peak Area with Peak Height at Different Element Concentrations in Lake Superior Water

Element	Total element concentration, ng/L[a]	Mean peak area, pV·s	Mean peak height, mm[b]	Coefficient of correlation[b]
Cu	0	898 (91)	8 (89)	
	1	91003 (5.0)	93 (5.0)	0.999
	10	1054405 (2.5)	868 (1.8)	0.999
Pb	0	1210 (60)	9 (33)	
	0.8	139000 (18.4)	134 (10.5)	0.971
	10	2055559 (8.5)	1893 (6.6)	0.996
Cd	0	419 (162)	3 (62)	
	0.06	10355 (8.4)	80 (7.1)	0.981
	0.7	125268 (4.1)	902 (4.6)	0.998

[a] 100-μL injections. Concentration 0 refers to instrument blank. [b] Peak area vs peak height correlation from linear least squares fit comprised of 10 instrument atomization blanks and 10 replicate atomization signals at the specified concentration. [c] Normalized to highest scale expansion. ( ) Indicates relative standard deviation for the mean of 10 replicates.

(32 Hz) was checked by obtaining 10 representative peak areas and comparing them in a linear least squares fashion against corresponding peak heights. Experiments were performed at two different concentrations; one approximately 5–7 times above the working limit of instrumental detection and the other about 10 times higher (Table I). Relative standard deviations were in expected ranges (2). Coefficients of correlation in all cases were close to 1; correlations were lower and relative standard deviations were higher for the lower concentrations, particularly for lead.

It is noted, however, that reproducibility may be slightly poorer than indicated, depending on operating conditions. The peak integration calculations are such that the area depends on the system drawing the baseline from a point at the beginning of atomization when a predetermined slope threshold is exceeded to the nearest point further in time when the slope threshold is again not exceeded. The practicalities of FAAS are such that slight "tailing noise" peaks can sometimes and unpredictably be present, especially when routinely working near detection limits. These might be best described as small superimposed peaks of negligible area immediately following the main atomization peak before the time it reaches baseline. They will often not affect peak height, but under those circumstances the complete area under the peak will not be obtained because of the manner in which the baseline is drawn. Therefore, a low result might be calculated. To circumvent this, appropriate precautions were always taken to assure that well-formed sampling atomization signals were obtained, such as employing only graphite tubes in good condition.

Use of this instrumental configuration for the analysis of these and other elements for more than a year's time has demonstrated a high degree of performance and efficiency. Hardware additions and the design of post-run calculation programs are generally applicable to other data systems capable of accurately integrating rapid atomization signals, having a suitable method for output of peak data, and possessing sufficient memory for BASIC. In addition, it is noteworthy to state that a newly available commercial automatic sampling system (Perkin-Elmer, Model AS-1) is essentially compatible with this system's configuration. The programs written for this work are available from the author on request.

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Solid State Programmable Switching Device for Semiautomated Multichannel Gas Analyses with Nondispersive Infrared Spectrometers

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Nondispersive infrared spectrometry has been widely applied in the field of gas analysis in recent years. Some typical uses include monitoring industrial and automotive emissions such as SO_2, NO, various hydrocarbons, HF, NH_3, organic acids, CO_2, CO, and H_2O, as well as anesthetic and associated gases in operating rooms. Nondispersive infrared analyzers (NDIR) are particularly adaptable to continuous process monitoring as well as remote, mobile sampling due to the simplicity and ruggedness incorporated in their design (1–4). NDIR instruments available from Beckman Instruments (Models 864, 865, and LB-2), Mines Safety Appliances (Models 303 and 309), Anarad, Inc. (Models AR-600, AR-500,